



Europäisches  
Patentamt

European  
Patent Office

Office européen  
des brevets

REC'D 23 DEC 2004

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03257647.2

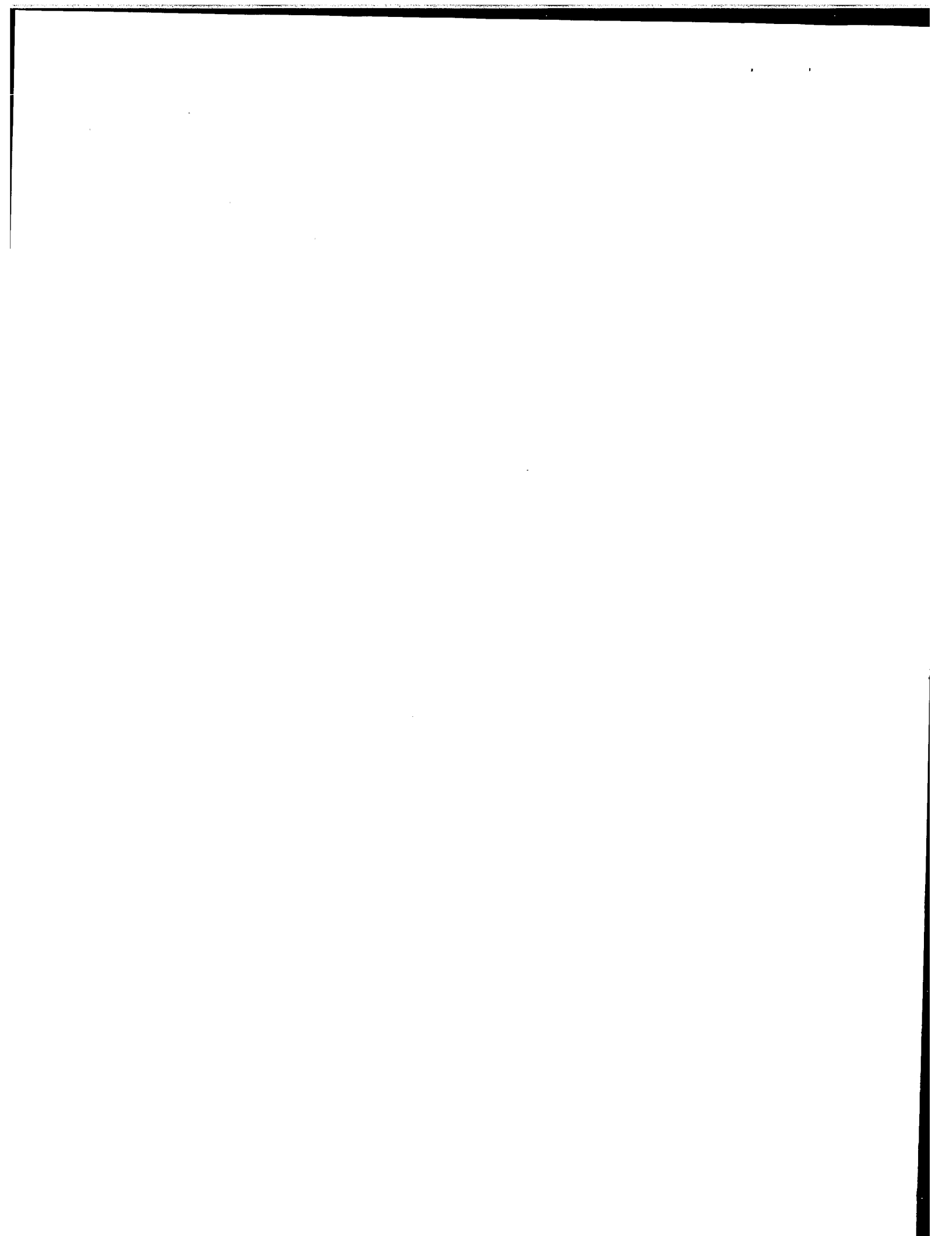
**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

R C van Dijk





PCT/EP2004 / 012755

Anmeldung Nr:  
Application no.: 03257647.2  
Demande no:

Anmeldetag:  
Date of filing: 04.12.03  
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Unilever Plc  
Unilever House,  
Blackfriars  
London,  
Greater London EC4P 4BQ  
GRANDE BRETAGNE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Shelf stable homogeneous suspension

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)  
revendiquée(s)  
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

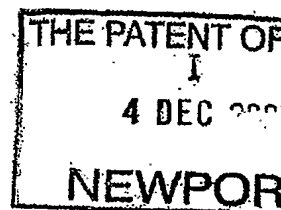
Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

A23C/

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL  
PT RO SE SI SK TR LI

• *Journal of Management Education* 32(10):1039-1050



Shelf stable homogeneous suspension

Field of the Invention

The invention relates to shelf stable homogeneous suspensions,  
5 especially milk drinks.

Background Art

Sterilization such as by ultra high temperature treatment of  
milk and other protein containing suspensions creates a product  
10 which is microbially stable at room temperature for several  
months. This preservation technique is especially used for  
drinks such as milk.

In general, a sterilization such as an Ultra High Temperature  
15 (UHT) treatment, raises the temperature of milk to over 125 °C  
for a few seconds, followed by rapid cooling. UHT-treated milk  
that is packaged aseptically results in a "shelf stable"  
product that does not require refrigeration until opened.

20 Although such products may be microbiologically stable for a  
long time, there may be some defects which limit the useful  
shelf life of these products. One of such defects that have  
been discussed extensively in the art is age gelation (also  
referred to as age thickening).

25

Age gelation is an aggregation phenomenon that affects shelf-  
stable, sterilized protein containing products, such as  
concentrated milk and UHT milk products and other dairy  
products. After weeks to months storage of these products,  
30 there is an increase in viscosity accompanied by visible  
gelation. This may be caused by aggregation of proteins leading  
to formation of a three-dimensional network. The exact  
mechanism underlying age gelation is not yet fully understood

but it was found that it may be at least partially caused by the proteolytic breakdown of proteins such as the casein in dairy products. It has been described in the art that bacterial or native plasmin enzymes that are resistant to heat treatment may induce the formation of a gel. Another factor that is often cited in relation to age gelation is temperature of storage of the sterilized suspension. Also chemical reactions may be responsible for age gelation.

WO-A-00/64267 discloses that the major problem for shelf stable milk is age gelation. This document suggests that use of food-grade polyphosphates having at least six phosphate groups, such as sodium hexametaphosphate in calcium-fortified milk and dairy-based products prevents age gelation of UHT treated milk.

15

The stability of homogeneous suspensions is also addressed in EP-A-1059851. This document teaches that a stable suspension can be made without emulsifiers by the inclusion of a thickener.

20

Although the above-cited prior art may offer some improvement to the stability of UHT treated products, further improvement and alternatives thereto are desired.

Therefore it is an object of the invention to provide a shelf stable sterilized protein containing suspension which uses alternative means of stabilisation.

#### Summary of the invention

30

We have surprisingly found that the addition of a small amount of emulsifier reduces the age gelation of sterilized protein containing suspensions.

- 5 Therefore the invention relates to a sterilized aqueous suspension comprising protein and fat or a fat replacer and from 0.01 wt% to 1 wt% emulsifier with a hydrophylic/lypophylic balance of at or below 16.
- 10 In a further aspect the invention relates to use of an emulsifier to reduce age gelation in sterilized protein containing suspensions, especially UHT treated milks.

Detailed description

15

In the context of the invention milk is preferably of dairy origin but the term milk also encompasses reconstituted dairy and non dairy milk and melanges, whereby the origin of protein, fat and other ingredients may be dairy, vegetable, marine or a  
20 combination thereof.

Where weight percentages are used they are based on total product weight unless otherwise is indicated.

- 25 In the context of the invention sterilization may be achieved by any suitable method such as Ultra High Temperature treatment (UHT), or long time high temperature treatment such as 30 minutes at a temperature of around 110 °C. In the context of the invention, the term sterilization also covers extended  
30 shelf life treatments which use temperatures over 110 °C. The preferred method of sterilization is UHT treatment. In the context of the invention, sterilization is defined as the heat treatment aimed at killing micro-organisms, including bacterial

spores. Preferred sterilization treatments are e.g. 30 min at 130 degrees C, or 1 s at 145 degrees C. To estimate the minimal heat treatment necessary, a factor  $f_0$  is commonly used, which is a measure of the total heat load that the product has seen.

5 It is commonly accepted that an  $f_0$  of 3 is the minimum heat load necessary to kill the most heat resistant bacteria. As an example: at 121 degrees C, an  $F_0$  of 3 means a heating time of 3 minutes.

In the context of the invention, UHT treatment is defined as  
10 treatment at a temperature of over 120 °C.

The products according to the invention are suspensions comprising a protein. Without wishing to be bound by any theory, it is believed that the protein is at least partly  
15 responsible for the phenomenon of age gelation in UHT treated suspensions.

The aqueous suspension preferably comprises from 0.5 to 10 wt%, more preferred from 1 to 5 wt%, even more preferred from 2 to 4 wt%. It will be appreciated that the level of protein is among  
20 others determined by the physical characteristics of the product in which it is applied. More viscous products generally comprise a higher protein level.

The protein may be of any origin such as vegetable origin, e.g.  
25 soy protein, or dairy protein.

Preferably the protein is a dairy protein because this is the protein imparting the desired taste, flavour and texture to milk.

30 The suspensions are stabilised by the addition of emulsifier. The emulsifier is an emulsifier which has a hydrophylic lypophylic balance value (HLB value) of at or below 16. The HLB value is a parameter which is describing the solubility of the



surfactant. The HLB value is a concept introduced by Griffin in 1950 as a measure of the hydrophilicity or lipophilicity of nonionic surfactants. It can be determined experimentally by the phenol titration method of Marszall; see "Parfumerie, Kosmetik", Vol. 60, 1979, pp. 444-448; and Rompp, Chemistry Lexicon, 8th Edition 1983, p. 1750. According to the invention, emulsifiers with an HLB value at or below 16 are to be understood as hydrophobic emulsifiers.

10 It has been found that emulsifiers with an HLB over 16, do not lead to the desired stabilization against age gelation. Optionally such emulsifiers with HLB values of more than 16 may be present in addition to the emulsifiers with HLB values at or below 16.

15

Preferably the emulsifier has an HLB value of below 14, more preferred from 1 to 10, more preferred from 2 to 9, most preferred from 3 to 6.

20 We have found that emulsifiers with HLB of at or below 14 are most effective in reducing age gelation. However also other emulsifiers such as Tween 20™ (polyoxyethylene sorbitan monolaurate) have a reducing effect on age gelation. This effect may be strengthened by the presence of another effective  
25 agent such as polyphosphate. Therefore in an alternative embodiment the product comprises an emulsifier with HLB of more than 14 but at or below 16, in combination with a polyphosphate.

30 The emulsifier is preferably selected from the group comprising monoglycerides, lecithins, diglycerides or a combination thereof. The most preferred emulsifier is monoglyceride,

especially saturated monoglycerides. Example of such emulsifiers are Hymono™ 8903 and Dimodan™ hp.

In the context of the invention proteins are not included in the term emulsifier.

5

The amount of emulsifier is dependent on the type of emulsifier selected and the relative amount of protein present, but generally the level of emulsifier is from 0.01 to 1 wt%, more preferred from 0.05 to 0.5 wt%, even more preferred from 0.05  
10 to 0.2 wt%.

In a preferred embodiment the total level of emulsifier, including the emulsifier that may be naturally present in the products, such as in milk, is from 0.05 to 1 wt%.

15

In an alternative embodiment, the emulsifier is a lecithin, wherein the total amount of lecithin, including phospholipids naturally present in the product, is from 0.05 to 1 wt%, more preferred from 0.07 to 0.5 wt%.

20

In a preferred embodiment, the emulsifier is a monoglyceride which is present in an amount of from 0.01 to 0.08 wt% on total product weight. This level includes the amount of monoglyceride which may be naturally present in the product such as milk  
25 wherein the average level of naturally present monoglyceride is generally around 0.004 wt%.

The aqueous suspension comprises fat or a fat replacer. The fat may be of any origin. It is preferred that the fat is dairy fat  
30 or a vegetable fat or a combination thereof.

In those embodiments where the fat is a vegetable fat, the fat is preferably selected from the group comprising sunflower oil, rapeseed oil, soy bean oil, olive oil, linseed oil or a combination thereof. The most preferred fats have a  
5 polyunsaturated fatty acid (PUFA) content of at least 30 wt% PUFA on total triglyceride composition.

The amount of fat is preferably from 0.1 to 8 wt%, more preferred from 1 to 5 wt%.

10

Optionally the products comprise a fat replacer. The fat replacer is preferably selected from the group comprising sucrose polyesters, phytosterols or esters thereof, including their saturated stanol equivalents or a combination thereof.

15

It has surprisingly been found that the addition of an emulsifier, especially monoglyceride in the described amount, to a suspension comprising fat and a phytosterolester increases the stability against age-gelation of these products to a  
20 surprisingly high level.

Most preferred the aqueous suspension comprises a fat and a phytosterol or ester thereof.

25 Phytosterols, also known as plant sterols or vegetable sterols can be classified in three groups, 4-desmethylsterols, 4-monomethylsterols and 4,4'-dimethylsterols. In oils they mainly exist as free sterols and sterol esters of fatty acids although sterol glucosides and acylated sterol glucosides are  
30 also present. There are three major phytosterols namely beta-sitosterol, stigmasterol and campesterol. Schematic drawings of the components meant are as given in "Influence of

Processing on Sterols of Edible Vegetable Oils", S.P. Kochhar;  
Prog. Lipid Res. 22: pp. 161-188.

The respective 5 $\alpha$ - saturated derivatives such as sitostanol,  
5 campestanol and ergostanol and their derivatives are also  
encompassed in the term phytosterol.

Preferably the phytosterol is selected from the group  
comprising fatty acid ester of  $\beta$ -sitosterol,  $\beta$ -sitostanol,  
10 campesterol, campestanol, stigmasterol, brassicasterol,  
brassicastanol or a mixture thereof.

The phytosterols in this preferred embodiment are preferably  
esterified with a fatty acid. Preferably the sterols are  
15 esterified with one or more C<sub>2-22</sub> fatty acids. For the purpose  
of the invention the term C<sub>2-22</sub> fatty acid refers to any  
molecule comprising a C<sub>2-22</sub> main chain and at least one acid  
group. Although not preferred within the present context the C<sub>2-</sub>  
22 main chain may be partially substituted or side chains may be  
20 present. Preferably, however the C<sub>2-22</sub> fatty acids are linear  
molecules comprising one or two acid group(s) as end group(s).  
Most preferred are linear C<sub>8-22</sub> fatty acids as occur in natural  
oils.

25 Suitable examples of any such fatty acids are acetic acid,  
propionic acid, butyric acid, caproic acid, caprylic acid,  
capric acid. Other suitable acids are for example citric acid,  
lactic acid, oxalic acid and maleic acid. Most preferred are  
myristic acid, lauric acid, palmitic acid, stearic acid,  
30 arachidic acid, behenic acid, oleic acid, cetoleic acid, erucic  
acid, elaidic acid, linoleic acid and linolenic acid.

When desired a mixture of fatty acids may be used for

esterification of the sterols. For example, it is possible to use a naturally occurring fat or oil as a source of the fatty acid and to carry out the esterification via an interesterification reaction.

5

Preferably the suspensions comprise a thickener. This thickener preferably contributes to the physical stability of the suspension. In a preferred embodiment the thickener is selected from the group comprising carrageenan, locust bean gum,  
10 xanthan, pectins, gum arabic, gelatin, guar gum, or a combination of any of these. Suitable amounts of thickener are in the range of from 0.005 to 0.5 wt%, preferably from 0.01 to 0.1 wt%.

15 In a preferred embodiment, the suspensions additionally comprise a multivalent metal ion such as calcium.

The suspension optionally comprises further ingredients. Examples of such ingredients are benefit agents such as live bacteria of the type of e.g. lactobacillus, or vitamins;

20 stabilising agent such polyphosphate, colouring agents, flavour agents, herbs, fruit pieces, fruit pulp, herb or fruit concentrate, fruit juice, anti-oxidants, sequestering agents, salts.

25 The suspension may be prepared from it's ingredients such as e.g. a reconstituted milk but it is preferred that the suspension is a natural product such as a dairy milk to which the emulsifier is added.

30 In a preferred embodiment, the invention relates to a milk, comprising from 0.1 to 5 wt% fat, from 0.01 to 0.2 wt% monoglyceride and from 0.2 to 4 wt% phytosterolester.

The fat in these milks may be from dairy or vegetable origin or a combination of these.

The suspension may be used as such or may be part of another  
5 composition such as a food product. It is preferred that the suspension is used as such. Even more preferred the suspension is a milk or a juice, most preferred a milk.

In a further aspect the invention relates to use of an  
10 emulsifier with HLB value at or below 16 to reduce age gelation in sterilized protein containing suspensions, especially UHT treated milks.

The invention is illustrated by the following non limiting  
15 examples.

### Examples

Generation

20

Determination of age gelation/stability

Age gelation is determined by eye by a panel of at least 5  
persons. The milk turns from liquid (pourable without visual  
25 lumps) to a soft gel, in some cases by the development of small lumps of protein. The age gelation is identified on basis of the following questions:

1. Is there a liquid layer on top which is greenish or less turbid than milk? (yes/no)
- 30 2. Is there inhomogeneity when pouring out the milk? (yes/no)
3. Do you see visible lumps? (yes/no)
4. Do you hear lumps falling while pouring the milk? (yes/no)

5. Is there a Tofu/custard like structure at the bottom?  
(yes/no)

Example 1

5

Carrageenan and monoglyceride (E471, Hymono™) were added to semi skimmed milk (fat content 1.5 wt% dairy fat, protein content 3.2 wt%), under agitation and mixed for 10 minutes. The amount of carrageenan was 0.01 wt% and the amount of  
10 monoglyceride was 0.1 wt% and 0.5 wt% sitosterolester of sunflower oil was added.

The milk was preheated to 70 °C and ultra high temperature treated at 143°C for 6 seconds by steam injection, then cooled  
15 to 70 °C, and homogenised at this temperature at about 200 bar. The milk was cooled to 15 to 20 °C and aseptically filled in aseptic tetrapaks™ and stored at ambient temperature (20 to 25 °C).

20 After 8 weeks at ambient temperature the milks were compared to milks with the same composition except that monoglyceride was left out or included at a level of only 0.001 wt%. These comparative milks were prepared by the same process.

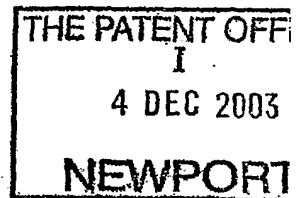
25 It was observed by eye by an expert panel of 5 people that the milks with monoglycerides in an amount of 0.1 wt% did not show any age gelation after a period of 8 weeks. A few lumps became visible after 8 months. The comparative products both showed lumps and a cream layer on top after a storage time of 4 weeks.  
30 For the comparative products, especially question (1) (Is there a liquid layer on top which is greenish or less turbid than milk?) was answered in the affirmative which pointed to a less desired product.

Example 2

Products were prepared according to the process and composition 5 of example 1. Together with the addition of carrageenan and 0.05 wt% monoglyceride, 0.7 wt% sitosterolester of sunflower oil was added.

The resulting products were found to be stable by a panel of 5 10 persons after storage for 8 weeks at a temperature of 20 to 25 °C.

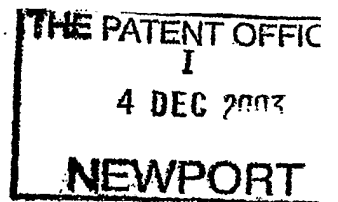




**Claims**

1. Sterilized aqueous suspension comprising protein and fat or a fat replacer and from 0.01 wt% to 1 wt% emulsifier with a hydrophylic/lipophylic balance of at or below 16.
2. Aqueous suspension according to claim 1 comprising from 0.5 to 10 wt% protein.
3. Aqueous suspension according to any of claims 1-2 wherein the protein is a dairy protein.
4. Aqueous suspension according to any of claims 1-3 wherein the emulsifier is selected from the group comprising monoglycerides, lecithins, diglycerides or a combination thereof.
5. Aqueous suspension according to any of claims 1-4 wherein the emulsifier is a monoglyceride.
6. Aqueous suspension according to any of claims 1-5 wherein the amount of emulsifier is from 0.05 to 0.2 wt%.
7. Aqueous suspension according to any of claims 1-6 comprising from 0.1 to 8 wt% fat.
8. Aqueous suspension according to any of claims 1-7 comprising a phytosterol.
9. Use of an emulsifier with HLB value at or below 16 to reduce age gelation in sterilized protein containing suspensions.





Abstract

Protein-containing suspensions such as milk that are preserved by a UHT treatment, show age gelation. This age gelation can be reduced by inclusion of an emulsifier with an HLB value below 16.

**PCT/EP2004/012755**

